Development of GaAs Infrared Window Material

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DEVELOPMENT OF GaAs INFRARED WINDOW MATERIAL

Semi-Annual Report

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The metallurgical, analytical, electrical and optical properties of semi-insulating GaAs were further investigated. Optimization of the 10.6 micron optical absorption coefficient continued. The measurement equipment involving a CO_2 laser was improved so that the homogeneity of samples can be evaluated. Doping experiments in GaSb gave closely-compensated but not high resistivity material--the maximum resistivity observed at room temperature was one ohm-cm. Evaluation of large diameter castings showed the need for a more controlled freezing surface, and plans have been made which will make this feasible.

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1. INTRODUCTION

This report covers the period 1 December, 1970 - 31 May, 1971 for Contract N00014-70-C-0132, entitled "Development of GaAs Window Material." Previous work on this contract performed during the period 1 December, 1969 - 30 November, 1970 is covered in a Technical Summary Report, published in December 1970, hereinafter referred to as I (also reference 1). That report explains why semi-insulating GaAs was chosen as the primary candidate for high-power CO_2 laser windows. The preparation of suitable GaAs is described and the physical, electrical and optical properties discussed at length. The preparation and properties of GaSb as a potential specialized window material are also described. The extension of present growth techniques to yield larger diameter material was attempted.

During the second year's work the following aims apply:

(a) Identify causes of absorption in high-resistivity GaAs and optimize the growth conditions to give the lowest possible optical absorption coefficient at 10.6 microns and room temperature.

(b) Develop large diameter (2 - 3") high quality single crystal material.

(c) Develop new techniques to extend the diameter capability into the 12" region (polycrystalline initially, followed by single crystal).

(d) Prepare GaSb in a high resistivity form and investigate its electrical and optical properties.

The present report extends the previous work in the areas of analysis, the technique of making absorption measurements, the homogeneity of single crystal material and the properties of GaSb. The work on normal diameter GaAs is covered in sections 2 through 4, GaSb is covered in section 5, while the large diameter work is in section 6. The last section contains conclusions and details of work yet to be done.

2. CRYSTAL GROWTH; GaAs

The GaAs crystal growth program has been running at a reduced level while further electrical, optical and analytical work was performed. Of the few ingots prepared a high-resistivity ingot obtained by the liquid encapsulation technique was noteworthy.

The large diameter single crystal program has been actively pursued, with the equipment completely designed. Parts are now being procured and the puller is expected to be operational early in the next reporting period. This equipment has also been designed to be flexible enough to accommodate the casting experiments to be performed and this will be commented on in section 6.

3. ELECTRICAL AND ANALYTICAL PROPERTIES OF GaAs

The resistivity measurements continue to be routinely performed as needed in the manner outlined in I. The "undoped" ingot grown by the liquid encapsulation technique mentioned in the previous section had a resistivity of 7×10^7 ohm-cm at the top and 3×10^4 ohm-cm at the bottom. This type of resistivity variation along a closely compensated ingot has been noticed previously, particularly for those dopants that do not have very deep-lying impurity levels. Thus, previously grown Fe- and Ni-doped ingots had higher resistivities at the top than at the bottom. This means that since the transition metals have low distribution coefficients they are either being aided at the top by other impurities having distribution coefficients greater than one or the total impurity level toward the bottom is greater than any amount of dopant can overcome. The latter explanation is the more likely, especially in light of the modified Blanc-Weisberg model (see I, p. 12-13 and references 2 and 3).

The mass spectrometric analysis program that we have been performing for our production GaAs has recently been yielding some interesting results that promise to be directly applicable to this study. In particular, the resolution of the instruments has been adjusted in order to better detect certain types of impurities that have a known "mobility

killer" effect in undoped and lightly doped material. While it is too early to state anything definite it looks as though the impurities can be identified during the next reporting period and steps taken to eliminate them.

Although it was stated in I that no Cr precipitates were found in GaAs using the direct-imaging mass analyzer, the spatial resolution that could be achieved was only ~ 1 micron. Recently we have observed Ga inclusions in <110> oriented Cr-doped ingots whose effective growth speed exceeded 4 cm hr^{-1}. This suggests the possibility of very small Ga inclusions in some ingots and/or the possibility of impurity precipitation near or at such sites. The excellent optical absorption coefficient noted in the "undoped" ingot (see next section) is also a good indication that the Cr may be precipitating in some cases, since the best Cr results are about the same as the undoped case, but the worse are some three times higher (for the same resistivity).

A study will therefore be initiated to determine the effects of growth speed and orientation on impurity content and optical absorption coefficient. We have previously restricted these parameters to the [111] direction and ~ 2 cm hr^{-1} respectively.

4. OPTICAL PROPERTIES

The equipment formerly used to measure optical absorption coefficients at 10.6 microns has been extensively reworked. A new outer chamber has been built (see I, p. 25-28). The new sample chamber is now mounted on an X-Y mechanism giving height and lateral position adjustments. The sample can therefore be moved across the laser beam. In this manner homogeneity measurements can be performed within the experimental accuracy of the equipment.

The results obtained on new as well as previously measured samples are somewhat ambiguous, but there has been a tendency for the optical absorption coefficient to be larger at the periphery of a disc cut normally in the ingot growth direction than at the center. It should be stressed that this result is tentative since the small differences are very close to the experimental error. Such an effect is not undesirable since the power density in a typical laser beam is higher at the center--this would then lead to a more uniform heating of the window than if the window material were completely homogeneous, avoiding some of the defocusing and translational effects currently considered troublesome.

The magnitude of the absorption coefficients measured remains within the 0.01 to 0.02 cm^{-1} range except for occasional departures above and

below this. The undoped (but high resistivity) material had a value of 0.009 - 0.010 cm^{-1}. Therefore further attempts will be made to repeat the preparation of this type of material, and deliberate oxygen doping will be investigated (see also remarks in previous section about precipitation effects).

The optical properties of the large diameter cast material are covered in Section 6.

5. PREPARATION AND PROPERTIES OF GaSb

Several ingots of GaSb were prepared from non-stoichiometric melts by normal Czochralski growth as detailed in I. The liquid encapsulation technique was not used during this period. The atomic percentage of antimony in the starting melt was kept at 70 in order to keep the defect (p-type) carrier concentration in the mid $10^{18}cm^{-3}$ range.[1,4] All ingots were doped with Cr and Te. The amount of the latter was adjusted in an attempt to give n-type material containing less than $10^{17}cm^{-3}$ carriers. From the electrical and mass spectrometric results it would appear that the presence of the Cr and low level of Te involved is affecting the distribution coefficient of Te. Thus the best result to date is a level of 5 ppm of Te, which is about two times higher than needed. The Cr levels are generally similar to those observed in semi-insulating GaAs.

The electrical properties of these ingots are difficult to interpret simply, but they are basically n-type with low mobility--the "best" ingot had a resistivity ~1 ohm-cm. Due to the mixed conduction a multi-band Hall analysis would be needed to obtain more information on the carrier concentrations, but since the resistivity is the critical parameter here a combination of simple Hall effect and mass spectrometric analysis should continue to suffice.

Some progress has been made in reducing impurity levels by more careful

treatment of the starting materials. For example the levels of Si, Al and Ca are now in the less than 1 ppma range. The major n- and p-type impurities are now at a sufficiently low level that the dominant carriers are caused by the vacancies (p), Te (n) and Cr (deep levels--although this still has to be proved).

6. LARGE DIAMETER GaAs

The optical and metallurgical properties of the 3" diameter casting of GaAs described previously (I, pp. 33-36) were further investigated. The optical absorption coefficient at 10.6 microns of a thin piece cut from the bottom (first-to-freeze portion) was found to be quite variable, values between 0.03 and 0.11 cm^{-1} being recorded. Examination with an infra-red microscope showed the presence of small gallium inclusions, particularly at grain boundaries.

These results have encouraged the building of equipment which will give two different approaches toward the attainment of slow controlled freezing rates. The first approach is to actually pull ingots of large diameter, while the second involves casting but in a manner much closer to the traditional gradient freeze technique. The former should yield high quality single crystal material having properties close to the best of the normal diameter pulled ingots, while the latter should give larger diameter but polycrystalline material. With controlled freezing the optical properties of this large diameter cast material can also be expected to match the small diameter pulled ingots.

7. FUTURE WORK

The program of optimization of semi-insulating GaAs optical properties at 10.6 microns will continue. In particular the identification of impurities and defects responsible for the observed variation in optical absorption coefficient will be performed via optical, electrical and mass spectrometric measurements. Different growth directions, growth speeds and melt stoichiometries should give valuable information, particularly on the metallurgical properties. The large-diameter work will take the dual path outlined in Section 6. The doping experiments involving GaSb will be followed by optical measurements if high resistivities are achieved.

8. REFERENCES

1. A. G. Thompson, Technical Summary Report, Contract N00014-70-C-0132, December 1970.

2. J. Blanc and L. R. Weisberg, Nature 192, 155 (1961).

3. W. DeVilbiss, Ph.D. Thesis, University of Missouri, Columbia, Mo. (1968).

4. F. J. Reid, R. D. Baxter and S. E. Miller, J. Electrochem. Soc. 113, 713 (1966).